Intrinsic defect processes in Ca–Al–Fe–O cement-phase compounds

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Atomistic-scale computer simulations, based on the ionic model, have been used to study intrinsic defect processes in a range of Ca–Al–Fe–O cement-phase compounds. The simulations accurately reproduce the structures of this diverse set of materials and predict the large disorder observed between the aluminium and iron sublattices in C_4AF. Additionally, the calculations predict that the extent of intrinsic disorder varies considerably from material to material, as does the dominant mode of disorder. Finally, the calculations indicate that clustering of defects is likely to play an important role in the mass transport mechanisms of all the compounds studied. © *1999 Kluwer Academic Publishers*

1. Introduction

The impetus for studying defects in C_4AF (C = CaO, A = Al_2O_3, and F = Fe_2O_3) has been the direct influence the defects have on colouring in cement clinkers; however, defects in other cement phases have gone unstudied largely because they do not exhibit such overt effects. Since defects play important roles in transport phenomena, phase equilibria, and microstructural properties, information concerning defect processes in the other phases is clearly desirable. Unfortunately, determining intrinsic defect properties in oxides via experiment is often difficult because extrinsic defects dominate. Experiments on cement-phase oxides are complicated further by a complex formation chemistry, which results in highly variable concentrations of impurities, leading to variable extrinsic defect properties. Consequently, such experiments are often not practical in cement phases.

As an alternative, defect energetics of ionic materials can be predicted using computer simulation. Because of extensive relaxation and consequential symmetry breaking associated with point defects, computational resources are not sufficient to thoroughly characterize all disorder processes in these complex oxides using *ab initio* quantum mechanical techniques. Fortunately, with materials that are largely ionic, it is possible to use a Born-like model of the lattice. Then by employing the Mott-Littleton approximation, computation time is reduced sufficiently to allow a complete study of disorder while maintaining a physically meaningful description of the lattice. Although this computational method is less rigorous than many quantum mechanical methods, the integrity of the calculations is aided by using a single, consistent set of potentials that model several compounds that are related by composition. In addition, the use of a consistent set of potentials allows a more straightforward comparison of defect behaviours among related materials.

Other simulations on CaO [1], Al_2O_3 [2], and Fe_2O_3 [3] have shown (as does the present work) that disorder enthalpies are quite high, making observation very difficult. This alone may explain the limited amount of experimental data regarding intrinsic disorder in these materials. Quantitative experimental data only exists for Al_2O_3 [4, 5] and agrees well with the calculated disorder enthalpies; however, large uncertainties in the measurements illustrate the difficulty in measuring the low concentrations of defects associated with such high enthalpies. Research on C_4AF [6] has shown qualitatively that intrinsic defects are impurity controlled, which is indicative of high Schottky and Frenkel disorder enthalpies. Such a sparse amount of experimental data concerning intrinsic disorder in Ca–Al–Fe–O cement-phase compounds makes structural data the primary source for checking atomistic simulation parameters. Therefore, to extend defect calculations beyond those on CaO, Al_2O_3, and Fe_2O_3, it is pertinent to include C_4AF and as many other related structures as possible in order to provide additional structural feedback. It is then a simple matter to extend the disorder analysis to those materials, which include CA, C_2A, C_3A, CF, C_2F, CA_2, CA_6, and C_4AF.

2. Methodology

The extent of the disorder present in a material depends on the increase in enthalpy accompanying the creation of defects associated with the disorder. The concentrations of defects involved in disorder processes are described by the mass action equations, which depend on this increase in enthalpy. When the concentration of defects is small, the nonconfigurational entropy contribution to the mass action equation is negligible, and the defect behaviour of a material is effectively specified by the increase in enthalpy. The method used in this study determines the enthalpy of a defect by calculating the

interaction energy between a defect and an otherwise perfect lattice.

To calculate these energies, a Born-like model is used in which the ions assume their formal charges. In this approximation, the lattice energy arises from three sources: Coulombic interactions between ions, a shell model description of atomic polarisation, and an additional interaction between ion pairs described by parameterized short-range forces that account for electron cloud overlap and dispersion. In these calculations, the Coulombic forces are summed using Ewald's method to provide convergence. The shell model approximates atomic polarization by modelling each polarizable ion as a massless shell of charge Y that is able to move with respect to a massive core with charge X, subject to a restraining harmonic force constant k [7]. To represent the short-range interactions, ion pairs interact through Buckingham potentials

$$E(r) = A\,e^{-r/\rho} - C/r^6$$

where r is the distance between two atomic species (each cation–anion pair and the anion–anion pair) and A, ρ, and C are adjustable parameters. The magnitude of this interaction falls off quickly with increasing r, and only ions separated within a certain cut-off distance (17.52 Å in this study) are considered.

The short-range potential parameters are determined by varying their values until the predicted lattice parameters match experimental data. In each case, the predicted structure is that which minimizes the total energy of the perfect lattice. Conventionally, a parameter set is fitted for each material, reproducing the structure as well as possible and closely reproducing dielectric and elastic constants. Such parameters are optimized for specific ion coordinations and bond lengths, and shifts away from equilibrium, such as those associated with relaxation around intrinsic defects, may be underestimated. Since defect enthalpies are greatly affected by distortions in the crystal immediately around the defects, this can lead to errors in the predicted defect enthalpies. Thus, a parameter set that can describe the potential energy surface away from equilibrium is required. This is achieved by deriving a single, consistent set of short-range potential parameters simultaneously fitted to a large number of related materials with differing cation-oxygen coordinations and bond lengths. The resulting parameters still reproduce individual structures well, and one may better compare relative disorder enthalpies of the various materials.

The perfect lattice energy is determined by starting with the experimentally determined structure and then adjusting both ion positions and lattice vectors, using the Newton-Raphson minimization procedure, until each ion experiences zero force. To calculate the enthalpy of a defect, such as a vacancy, an interstitial ion, or a substitutional ion, the Mott-Littleton approximation is used [8]. This method begins with the relaxed perfect lattice and then places a defect in the centre of a spherical region I. All ion positions in region I are allowed to relax in response to the defect, and interactions are summed over all pairs of ions within the region. The radius of region I in these calculations is

11.68 Å. Larger radius values than this make negligible difference to predicted defect energies. The outer region, region II, extends to infinity, and the interaction of the region II ions with the lattice defect is treated as a dielectric response in accord with the Mott-Littleton approximation. To ensure a smooth transition between regions I and II, an interfacial region, region IIa, is introduced. Ion positions within region IIa are allowed to vary, minimizing interactions between all ions in region I and minimizing the Mott-Littleton response in region II. The region IIa radius in these calculations is 29.6 Å, and the whole procedure is executed with the CASCADE code [9].

3. Results and discussion

Essential to the defect modelling process are well-parameterized, short-range potentials. As such, the short-range potential parameters and their ability to reproduce the experimentally observed structures are presented first. Subsequently, the intrinsic disorder enthalpies are reported. Each of these enthalpies is determined by summing the calculated enthalpies of defects that are components of the corresponding defect reaction. Finally, stabilities of clusters comprised of intrinsic defects are listed in terms of cluster binding energies.

3.1. Perfect lattice calculations

The set of potentials used in this study are summarized in Table I. Some are adopted from previous works, while others are derived specifically for this work. These parameters model the experimental structures well, giving a good foundation for the defect study.

The O^{2-}–O^{2-}, Al^{3+}–O^{2-}, and Fe^{3+}–O^{2-} potentials have been developed in other studies. The O^{2-}–O^{2-} potential has been used successfully to model a wide range of materials including CeO_2 surfaces [10], $SrTiO_3$ interfaces [11], intrinsic defects in $ZnCr_2O_4$ [12], ZnO–In_2O_3 intergrowth structures [13], and defects in β–Al_2TiO_5 [14]. The extent to which the O^{2-}–O^{2-} potential is successful emphasizes how well it encompasses very diverse crystallographic environments.

TABLE I Potential parameters

Short-range potentials				Reference
O^{2-}–O^{2-}	A	9547.96	eV	[2, 10–15]
	ρ	0.21916	Å^{-1}	
	C	32.0	eVÅ^6	
Al^{3+}–O^{2-}	A	1725.2	eV	[2]
	ρ	0.28971	Å^{-1}	
	C	0.0	eVÅ^6	
Fe^{3+}–O^{2-}	A	1414.6	eV	[15]
	ρ	0.3128	Å^{-1}	
	C	0.0	eVÅ^6	
Ca^{2+}–O^{2-}	A	1186.48	eV	this work
	ρ	0.339	Å^{-1}	
	C	0.0	eVÅ^6	
Shell model parameters				
Oxygen	Y	−2.80	$|e|$	[2]
	X	0.80	$|e|$	
	k	54.8	eVÅ^{-2}	

TABLE II Summary of structural parameters[a]

Compound	Property	Calculated	Observed	Percent agreement	Reference
Al$_2$O$_3$	a (Å)	4.8110	4.7628	101.01	[18]
	c (Å)	12.7316	13.0032	97.91	
	c/a	2.65	2.73	97.07	
	u	0.352	0.352	100.00	
	v	0.306	0.309	100.98	
Fe$_2$O$_3$	a (Å)	5.048	5.035	100.27	[18]
	c (Å)	13.35	13.72	97.34	
	c/a	2.64	2.72	97.06	
	u	0.355	0.353	99.44	
	v	0.3	0.306	102.00	
CaO	a (Å)	4.8104	4.8105	100.00	[19]
CA	a (Å)	8.789	8.700	101.02	[20]
	b (Å)	8.046	8.092	99.43	
	c (Å)	15.602	15.191	102.71	
	β (°)	90.54275	92.28333	100.29	
C$_2$A	a (Å)	5.46	5.23	104.48	[21]
	b (Å)	14.41	14.45	99.71	
	c (Å)	5.32	5.41	98.39	
C$_3$A	a (Å)	15.430	15.263	101.10	[22]
CA$_2$	a (Å)	13.0149	12.8398	101.36	[23]
	b (Å)	9.0946	8.8624	102.62	
	c (Å)	5.4206	5.4311	99.81	
	β (°)	108.4325	106.8333	101.50	
CA$_6$	a (Å)	5.606	5.564	100.75	[24]
	c (Å)	21.685	21.892	99.05	
CF	a (Å)	9.18	9.23	99.44	[25]
	b (Å)	10.724	10.705	100.18	
	c (Å)	3.024	3.024	100.00	
C$_2$F	a (Å)	5.4776	5.4253	100.96	[26]
	b (Å)	14.6963	14.7687	99.51	
	c (Å)	5.610	5.598	100.21	
C$_4$AF	a (Å)	5.592	5.598	99.89	[17]
	b (Å)	14.5	14.6	99.31	
	c (Å)	5.4266	5.4253	100.02	

[a]significant figures from references.

TABLE III Predicted unit cell volumes

Compound	Calc. volume/exp. volume (%)
Al$_2$O$_3$	99.91
Fe$_2$O$_3$	97.86
CaO	100.00
CA	103.16
C$_2$A	102.50
C$_3$A	103.32
CA$_2$	102.90
CA$_6$	100.55
CF	99.60
C$_2$F	100.68
C$_4$AF	99.23

Two oxygen shell model parameter sets associated with this O^{2-}–O^{2-} potential already exist, and the set in Table I is the one that best reproduces the mixed oxide structures in this work. The Al^{3+}–O^{2-} parameters were derived by fitting to the Al$_2$O$_3$, MgAl$_2$O$_4$, Al$_2$TiO$_5$, and Ca$_3$Al$_2$O$_6$ structures using the above O^{2-}–O^{2-} potential, providing varied cation–oxygen coordinations and separations [2]. Likewise, the Fe^{3+}–O^{2-} potential was fitted to α–Fe$_2$O$_3$, β–Fe$_2$O$_3$, Fe$_3$O$_4$, ZnFe$_2$O$_4$, and MgFe$_2$O$_4$ [15].

The Ca^{2+}–O^{2-} potential parameters are refined from those used in earlier studies [2, 16] by fitting to the structures of CaO, CA, C$_2$A, C$_3$A, CF, C$_2$F, and C$_4$AF. The predicted structural data and its agreement with experimental data are presented in Table II. The accuracy of the defect enthalpies depends foremost on unit cell volume, which is therefore a critical indicator of the quality of a parameter set. The volume agreement, shown in Table III, is good, especially considering the diversity of structures modelled by this single set of potentials.

3.2. Intrinsic disorder

With the perfect lattice enthalpies determined, the change in enthalpy accompanying the presence of defects is calculated. The individual defect enthalpies are not listed; rather, the enthalpies of Schottky disorder (cation and anion vacancies in stoichiometric ratios), Frenkel disorder (ion interstitial–vacancy pairs), and anti-site disorder (exchange of cation species between lattice sites) are reported. In each case, the reaction enthalpies are tabulated assuming that the component defects are spatially isolated from each other. The effect of defect clustering is considered in a later section.

Disorder reaction enthalpies are reported in electron volts per defect (1 eV $= 1.603 \times 10^{-19}$ Joule). The significance of a disorder reaction is judged according to the resulting concentrations of defects, which are related to the formation enthalpy through standard mass action equations. For example, in CaO the concentrations of defects associated with the Schottky reaction are given by

$$[V_O^{\cdot\cdot}][V_{Ca}''] = e^{-\Delta h/kT}$$

where $[x]$ represents the concentration of species x, Δh is the total Schottky formation enthalpy, k is the Boltzmann constant, and T is the temperature in Kelvin. Since in CaO the Schottky reaction has the lowest enthalpy, it is the dominant mode of disorder. Consequently, at high temperatures one may assume

$$[V_O^{\cdot\cdot}] = [V_{Ca}''] = e^{-\Delta h/2kT}$$

Thus, a hypothetical, total Schottky reaction energy of 4.0 eV (2.0 eV per defect) in CaO would result in about 1 ppm oxygen vacancies and 1 ppm calcium vacancies at 1400 °C. In general, the exponent is divided by the number of defects involved in the reaction, and the division by two in the above equation is a specific instance of this. For this reason, the reaction enthalpies in Tables IV–VI are reported as eV per defect, and the relative importance of the various reactions can be assessed directly. For the temperatures at which cement clinkers are processed (i.e. 1300–1400 °C), reaction enthalpies above 3 eV per defect will not result in significant defect concentrations even in pure materials. Defects of reactions with enthalpies between 1 and 2 eV per defect are barely observable in pure material, and are easily obscured when even small concentrations of aliovalent impurities are present. Below 1 eV per defect, intrinsic defects can become important, even in the presence of impurities.

The results of Schottky disorder calculations are shown in Table IV, and the Frenkel disorder results

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TABLE IV Schottky disorder reaction enthalpies

Compound	Full Schottky (eV per defect)	Ca partial Schottky (eV per defect)	Fe partial Schottky (eV per defect)	Al partial Schottky (eV per defect)
Al_2O_3	5.78	—	—	—
Fe_2O_3	5.15	—	—	—
CaO	3.54	—	—	—
CA	4.51	3.80	—	4.68
C_2A	3.52	3.38	—	3.50
C_3A	3.15	2.19	—	4.22
CA_2	4.53	4.33	—	4.41
CA_6	5.72	3.89	—	3.90
CF	2.99	2.16	3.33	—
C_2F	3.30	3.02	3.48	—
C_4AF	3.52	3.09	3.98	3.65

TABLE V Frenkel disorder reaction enthalpies

Compound	Ca Frenkel (eV per defect)	Fe Frenkel (eV per defect)	Al Frenkel (eV per defect)	O Frenkel (eV per defect)
Al_2O_3	—	—	7.35	5.66
Fe_2O_3	—	6.78	—	5.02
CaO	5.64	—	—	5.70
CA	3.03	—	5.55	3.42
C_2A	5.08	—	6.07	2.20
C_3A	1.09	—	5.84	3.02
CA_2	3.16	—	5.01	2.87
CA_6	5.70	—	5.52	3.54
CF	5.67	7.09	—	4.59
C_2F	4.46	5.94	—	2.19
C_4AF	4.52	6.67	6.16	2.33

TABLE VI Anti-site disorder reaction enthalpies

Compound	Ca–Fe Anti-site (eV per defect)	Ca–Al Anti-site (eV per defect)	Fe–Al Anti-site (eV per defect)
CA	—	2.73	—
C_2A	—	1.71	—
C_3A	—	1.94	—
CA_2	—	3.60	—
CA_6	—	3.91	—
CF	1.71	—	—
C_2F	1.43	—	—
C_4AF	1.98	2.12	0.20

are shown in Table V. Schottky enthalpies are all too high to be of significance except possibly the Ca partial Schottky enthalpies of CF and C_3A. Like the Schottky disorder, most cation Frenkel enthalpies are also too high to be important except, most notably, the calcium Frenkel enthalpy in C_3A. Oxygen Frenkel disorder exhibits moderate enthalpies for C_2A, C_4AF, and C_2F; nevertheless, the calcium Frenkel reaction in C_3A is clearly more significant.

The results of anti-site disorder calculations are shown in Table VI. In CA, CA_2, and CA_6, anti-site disorder is of no significance whatsoever. In C_2A, C_3A, CF, C_2F, and C_4AF, Ca–Al and Ca–Fe anti-site disorder are roughly as significant as the lowest enthalpy Schottky and Frenkel reactions. In the case of Fe–Al anti-site disorder in C_4AF, the enthalpy is very low, indicating that this is the most significant intrinsic disorder in any of these materials. The predicted enthalpy is indicative of high disorder, which is in good accord with experimental data that indicates 24% disorder between the iron and aluminium sublattices [17].

3.3. Selected defect clusters

The importance of defect clusters containing intrinsic defects was studied for clusters containing three or fewer defects. The significance of a defect cluster is determined by its binding energy BE, defined as the gain in enthalpy when isolated defects form a cluster

$$BE_{cluster} = \left[\sum_{components} E_{defect} \right] - E_{cluster}$$

so more positive binding energies represent more stable clusters. The defect cluster enthalpy $E_{cluster}$ is determined by introducing the whole cluster into region I of the Mott-Littleton calculation.

The binding energies are divided into two tables—one for Schottky disorder related clusters and one for clusters associated with anti-site disorder. The binding energies of clusters relevant to Schottky disorder are substantial as shown in Table VII. The results from clusters involved in anti-site disorder are summarized in Table VIII. These clusters are less significant than the clusters involved in the Schottky processes. Overall, the binding energies calculated here are significant enough

TABLE VII Defect clusters associated with Schottky disorder

	Cluster binding energies (eV)				
Compound	$[V_O^{\cdot\cdot}:V_{Ca}'']^\times$	$[V_O^{\cdot\cdot}:V_{Fe}''']'$	$[V_O^{\cdot\cdot}:V_{Fe}''':V_O^{\cdot\cdot}]^\cdot$	$[V_O^{\cdot\cdot}:V_{Al}''']'$	$[V_O^{\cdot\cdot}:V_{Al}''':V_O^{\cdot\cdot}]^\cdot$
Al_2O_3	—	—	—	3.72	8.92
Fe_2O_3	—	3.25	7.96	—	—
CaO	0.89	—	—	—	—
CA	1.63	—	—	5.21	8.59
C_2A	2.30	—	—	4.46	8.12
C_3A	1.07	—	—	3.97	8.10
CA_2	1.42	—	—	4.98	6.96
CA_6	1.42	—	—	4.14	6.24
CF	1.63	2.86	5.54	—	—
C_2F	1.99	4.27	7.71	—	—
C_4AF	2.07	4.22	6.78	4.46	8.26

TABLE VIII Defect clusters associated with anti-site disorder

Compound	Cluster binding energies (eV)		
	$[Ca'_{Fe}:Fe^{·}_{Ca}]^{\times}$	$[Ca'_{Al}:Al^{·}_{Ca}]^{\times}$	$[Fe^{\times}_{Al}:Al^{\times}_{Fe}]^{\times}$
CA	—	0.60	—
C_2A	—	0.85	—
C_3A	—	1.01	—
CA_2	—	4.26	—
CA_6	—	1.27	—
CF	0.33	—	—
C_2F	0.82	—	—
C_4AF	0.71	1.15	0.01

to markedly influence transport in these materials with the transport species becoming trapped in the form of such clusters. The results also suggest that the formation of clusters is important for the solution of oxides in cement phase materials.

4. Conclusions

Atomistic-scale simulation has provided information that would be otherwise impractical to obtain about defect processes in Ca–Al–Fe–O cement-phase compounds. This was made possible by employing a consistent set of potentials that accurately reproduce the variety of structures found in this set of materials. The following summarizes the observations made using this technique.

1. For most of the materials studied, intrinsic Schottky and Frenkel enthalpies are so high that these types of disorder reactions are not important. The most notable exception to this is calcium Frenkel disorder in C_3A. Additionally, calcium Schottky disorder in CF and C_3A, and oxygen Frenkel disorder in C_2A, C_4AF, and C_2F may be of minor significance as compared with extrinsic disorder brought about by impurities.

2. The very low Al–Fe anti-site enthalpy calculated for C_4AF is in good agreement with the large degree of sublattice disorder observed by experiment.

3. The enthalpies associated with Ca–Fe and Ca–Al anti-site disorder throughout these materials are moderately high, indicating that this disorder is only of minor importance.

4. Binding enthalpies are generally high, implying that any impurity ions would become associated into clusters. This has important implications for the transport of ions through these lattices.

Acknowledgements

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